

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C07F 17/00, C08F 10/00, 4/60	A1	(11) International Publication Number: WO 97/10248 (43) International Publication Date: 20 March 1997 (20.03.97)
(21) International Application Number: PCT/EP96/03952 (22) International Filing Date: 10 September 1996 (10.09.96) (30) Priority Data: 08/526,376 11 September 1995 (11.09.95) US (60) Parent Application or Grant (63) Related by Continuation US 08/526,376 (CIP) Filed on 11 September 1995 (11.09.95) (71) Applicant (for all designated States except US): MONTELL TECHNOLOGY COMPANY B.V. [NL/NL]; Hoeksteen 66, NL-2132 MS Hoofddorp (NL). (72) Inventors; and (75) Inventors/Applicants (for US only): EWEN, John, A. [US/US]; 14311 Golf View Trail, Houston, TX 77059 (US). STROZIER, Robert, W. [US/US]; 5611 Hazen Street, Houston, TX 77081 (US). JONES, Robert, L., Jr. [US/IT]; Via Carlo Mayr, 110, I-44100 Ferrara (IT). ELDER, Michael, J. [US/IT]; Corso della Giovecca, 140, I-44100 Ferrara (IT).		(74) Agent: ZANOLI, Enrico; Montell Italia S.p.A., Intellectual Property, Patents and Trademarks, Via Pergolesi, 25, I- 20124 Milano (IT). (81) Designated States: CA, JP, KR, RU, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: OPEN-PENTADIENYL METALLOCENES, PRECURSORS THEREOF AND POLYMERIZATION CATALYSTS THERE- FROM (57) Abstract New metallocene compounds are described where the ligand contains at least one open-pentadienyl containing radical characterized by a cyclic or acyclic, six π electron, delocalized, five atomic center structure. These metallocenes can advantageously be used in catalyst systems for the polymerization of olefins to generate a wide variety of different polymers including HDPE, LLDPE, ethylene/propylene/(diene) elastomers, tactiospecific C3+ α -olefin polymers, intimate mixture thereof and the like.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LJ	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

TITLE

**"OPEN-PENTADIENYL METALLOCENES, PRECURSORS THEREOF AND
POLYMERIZATION CATALYSTS THEREFROM"**

TECHNICAL FIELD OF THE INVENTION

This invention relates to a class of metal complexes including at least one open-pentadienyl (Op) ligand or group, to polymerization catalysts derived therefrom, and to the use of said catalysts for the polymerization of addition polymerizable monomers, particularly olefins. More particularly, the present invention relates to α -olefin polymerization processes to make atactic and/or tactiospecific homopolymers, atactic and/or tactiospecific copolymers, and/or random or block copolymers.

BACKGROUND OF THE INVENTION

Polymerization of vinyl monomer, both mono-olefins and conjugated dienes, has been focused on transition metal catalysts since the work of Ziegler and Natta. These catalysts are based on a central transition metal ion or atom surrounded by a set of coordinating ligands and modified by various co-catalysts. These polymerization systems when brought in contact with addition polymerizable monomers polymerize the monomers into polymers.

By controlling the nature of the ligand system, the central transition metal ion or atom and the co-catalyst, highly active catalytic agents can be made. In addition, catalysts can be made that yield polymers with high degrees of additions regularity and in the case of non-ethylene type monomers, stereoregularity or tactiospecificity.

U.S. Pat. No. 3,051,690 discloses a process of polymerizing olefins to controlled, high molecular weight polymers by the

controlled addition of hydrogen to a polymerization system that includes a hydrocarbon insoluble reaction product of a Group IVB, VB, VIB and VIII compound and an alkali metal, alkaline earth metal, zinc, earth metal or rare earth metal organometallic compound. It is further known that certain metallocenes such as bis(cyclopentadienyl) titanium or zirconium dialkyls in combination with aluminum alkyl/water cocatalyst form homogeneous catalyst systems for the polymerization of ethylene.

German Patent Application 2,608,863 discloses the use of a catalyst system for the polymerization of ethylene consisting of bis(cyclopentadienyl) titanium dialkyl, aluminum trialkyl and water. (Cyclopentadienyl is sometimes abbreviated as Cp.) While German Patent Application 2,608,933 discloses an ethylene polymerization catalyst system of the general formula $(\text{Cp})_n\text{ZrY}_{4-n}$ where n is a number from 1 to 4 and Y is a hydrocarbyl group or a metalloalkyl in combination with an aluminum trialkyl cocatalyst and water.

European Patent Appln. No. 0035242 discloses a process for preparing ethylene and atactic propylene polymers in the presence of a halogen-free Ziegler catalyst system of the general formula $(\text{Cp})_n\text{MeY}_{4-n}$ where n is an integer from 1 to 4, Me is a transition metal, especially zirconium, and Y is either hydrogen, a C1-C5 alkyl, metalloalkyl group or a other radical in combination with an alumoxane. While U.S. Patent No. 5,324,800 discloses a catalyst system for polymerizing olefins including a metallocene catalyst represented by the general formula $(\text{C}_5\text{R}'_m)_p \text{R}''_s (\text{C}_5\text{R}'_m) \text{MeQ}_{3-p}$ and $\text{R}''_s (\text{C}_5\text{R}'_m)_2 \text{MeQ}'$ where $(\text{C}_5\text{R}'_m)$ is a substituted Cp group and an alumoxane.

Polyolefins can be prepared in a variety of configurations that correspond to the manner in which each new monomer unit is added to a growing polyolefin chain. Four basic configurations are commonly recognized for polyolefins, atactic, hemi-isotactic, isotactic and syndiotactic. Of course, a given polymer may incorporate regions of each configurational type, yet not exhibit the pure or nearly pure configuration and polyethylene can have no tacticity.

Atactic polymers exhibit no regular order of repeat unit orientation in the polymer chain, i.e., the substituents are not regularly ordered relative to a hypothetical plane containing the polymer backbone (the plane is oriented such that the substituents on the pseudo-asymmetric carbon atoms are either above or below the plane). Instead, atactic polymers exhibit a random distribution of substituent orientations.

Besides metallocene catalysts that produce polyethylene and atactic polyolefins, certain metallocenes are also known to produce polymers with varying degrees of stereoregularity or tacticospecificity, such as isotactic, syndiotactic, and hemi-isotactic polymers which have unique and regular repeating stereochemistries or substituent orientations relative to the plane containing the polymer backbone.

Isotactic polymers are typically described as having the substituents attached to the pseudo-asymmetric carbon atoms oriented on the same side relative to the polymer backbone, i.e., the substituents are all either configured above or below a plane containing the polymer backbone. Isotacticity can be determined through the use of NMR. In Bovey's NMR nomenclature, an isotactic pentad is represented by " mmmm " with each "m" representing a "meso" dyad or successive monomer units oriented

with the substituents oriented on the same side relative to the polymer backbone. As is well known in the art, any deviation, disruption, or inversion about a pseudo asymmetric carbon in the chain will lower the degree of isotacticity and crystallinity of the polymer. In contrast, the syndiotactic structure is typically described as having the substituents, that are attached to the pseudo-asymmetric carbon atoms, pseudo-enantiomorphically disposed, i.e., the substituents are oriented alternately and regularly above and below the plane containing the polymer chain. Syndiotacticity can also be determined through the use of NMR. In NMR nomenclature, a syndiotactic pentad is represented by " rrrr " in which each "r" represents a "racemic" dyad, i.e., successive substituents on alternate sides of the plane. The percentage of "r" dyads in the chain determines the degree of syndiotacticity of the polymer.

There are other variations in polymer structures as well. One such variant is the so-called hemi-isotactic polymers. Hemi-isotactic polymers are ones in which every other pseudo-asymmetric carbon atom has its substituent oriented on the same side relative to the plane containing the polymer backbone. While, the other pseudo-asymmetric carbon atoms can have their substituents oriented randomly either above or below the plane. Since only every other pseudo-asymmetric carbon is in an isotactic configuration, the term hemi is applied.

Isotactic and syndiotactic polymers are crystalline polymers and are insoluble in cold xylene. Crystallinity distinguishes both syndiotactic and isotactic polymers from hemi-isotactic or atactic polymers that are soluble in cold xylene and are non-crystalline. While it is possible for a catalyst to produce all four types of polymers (atactic, hemi-isotactic, isotactic and

syndiotactic), it is desirable for a catalyst to produce predominantly or essentially polymer type with little or no other polymer type and few stereochemical defects.

Several catalysts that produce isotactic polyolefins are disclosed in U.S. Pat. Nos. 4,794,096 and 4,975,403, as well as European Pat. Appln. 0,537,130. Several catalysts that produce syndiotactic polyolefins are disclosed in U.S. Pat. Nos. 3,258,455, 3,305,538, 3,364,190, 4,852,851, 5,155,080, and 5,225,500.

Besides neutral metallocenes, cationic metallocenes are known to result in polymers with varying degrees of tactic specificity. Cationic metallocene catalysts are disclosed in European Patent Applications 277,003 and 277,004. Catalysts that produce hemi-isotactic polyolefins are disclosed in U.S. Pat. Nos. 5,036,034. In addition to monoolefins homopolymers, polymerization catalysts for preparing copolymers of monoolefins or polymers of di-functional olefins or copolymers of di-functional olefins and monoolefins can be prepared using coordinated metal catalysts including metallocene catalysts.

Although many metallocene catalysts are now available, the need for new ligand systems to make catalysts for the polymerization of olefins is still important and represents a significant advancement in the art. Such new ligand systems and the catalyst derived therefrom can offer new design approaches for making highly stereoregular or tactic specific polymers essentially free of defects, polymers with controlled defect statistics, copolymers with controlled properties, new approaches for molecular weight control and the control of other polymer properties.

Metal complexes containing a single non-aromatic, anionic, dienyl ligand group with a bridged ligand structure are described in International applications WO 96/08497 and WO 96/08498. Furthermore, group 4 metal complexes in the +2 or +3 formal oxidation state and containing non-aromatic, anionic, dienyl ligand groups are described in International application WO 96/16094. Those three applications were not published at the priority date of the present invention.

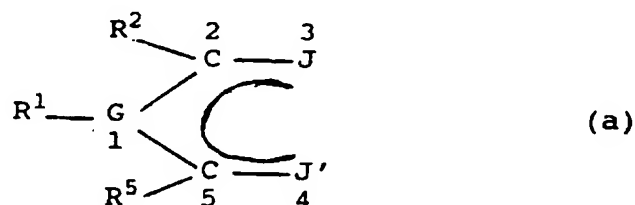
SUMMARY OF THE INVENTION

The present invention provides new open-pentadienyl containing metal complexes and catalysts derived therefrom for the polymerization of addition polymerizable monomers where the catalyst can be used to prepare polymer products with desired properties such as molecular weight, molecular weight distribution, density, tacticity and terminal unsaturation.

The catalysts of the present invention are useful for the polymerization of addition polymerizable monomers such as α -olefins to homopolymer and/or copolymers and comprise new metallocene catalysts optionally in combination with co-catalysts such as alumoxanes. The metallocenes of the present invention are organometallic coordination compounds of mono, di and tri-open-pentadienyl ligand systems and their transition metals coordinate complexes, especially complexes of a Group 3, 4, or 5 elements from the Periodic Table of Elements, or Lu, La, Nd, Sm, Gd, and the like.

Thus, according to a first aspect of the present invention, there are provided metal complexes represented by the general formula $YR^i_i Z_j MeQ_k P_l$ wherein:

- Y is an open-pentadienyl containing radical of the formula (a):



where G is a carbon atom, a nitrogen atom, a silicon atom or a phosphorus atom; J is a $\text{CR}^3\text{R}^{3'}$ radical, a $\text{SiR}^3\text{R}^{3'}$ radical, a $\text{NR}^{3''}$ radical, a $\text{PR}^{3''}$ radical, an oxygen atom or a sulfur atom and J' is a $\text{CR}^4\text{R}^{4'}$ radical, a $\text{SiR}^4\text{R}^{4'}$ radical, a $\text{NR}^{4''}$ radical, a $\text{PR}^{4''}$ radical, an oxygen atom or a sulfur atom and where J and J' can be the same or different; R^1 , R^2 , R^3 , $\text{R}^{3'}$, $\text{R}^{3''}$, R^4 , $\text{R}^{4'}$, $\text{R}^{4''}$, and R^5 can be the same or different and are a hydrogen atom, a linear or branched C1-C20 hydrocarbyl radical, a linear or branched C1-C20 halocarbyl radical, a linear or branched C1-C20 hydrohalocarbyl radical, a linear or branched C1-C20 alkoxy radical, a C3-C12 cyclohydrocarbyl radical, a C3-C12 cyclohydrohalocarbyl radical, an aryl radical, an alkylaryl radical, an arylalkyl radical, a silicon hydrocarbyl radical, a germanium hydrocarbyl radical, a phosphorous hydrocarbyl radical, a nitrogen hydrocarbyl radical, a boron hydrocarbyl radical, an aluminum hydrocarbyl radical or a halogen atom, or R^2 and R^3 , $\text{R}^{3'}$ or $\text{R}^{3''}$ and/or R^5 and R^4 , $\text{R}^{4'}$ or $\text{R}^{4''}$ can be joined together to form a 4 to 6 membered ring or a fused 6 to 20 membered ring system, or where R^3 , $\text{R}^{3'}$, or $\text{R}^{3''}$ and R^4 , $\text{R}^{4'}$, or $\text{R}^{4''}$ can be joined together so that the five numbered atonic centers making up the five centered delocalized six π electron ligand are contained in a 7 to 20 membered ring, or where R^3 , $\text{R}^{3'}$, or $\text{R}^{3''}$ and R^4 , $\text{R}^{4'}$, or $\text{R}^{4''}$ can be fused together so that the five numbered atonic centers making up the five centered

delocalized six π electron ligand are contained in a six membered ring;

- Z is the same of different Op containing radical, a Cp containing radical, a nitrogen containing radical, a phosphorous containing radical, an oxygen containing radical, a sulfur containing radical, or the like;
- R" is a C1-C20 alkenyl radical, a peralkylated C1-C20 alkenyl radical, a C3-C12 cyclohydrocarbyl radical, an aryl radical, a diaryl allyl radical, a silicon hydrocarbyl radical including a dihydrocarbyl silenyl radical, a germanium hydrocarbyl radical including a dihydrocarbyl germanium radical, a phosphorous hydrocarbyl radical including a phosphine radical, a nitrogen hydrocarbyl radical including an amine radical, a boron hydrocarbyl radical, an aluminum hydrocarbyl radical, or the like, and where R" structurally bridges the Y radical and a Z radical;;
- Me is a Group 3, 4, or 5 element from the Periodic Table of Elements, or Lu, La, Nd, Sm, Gd, or the like;
- Q is a C1-C20 hydrocarbon radical such as an aryl, alkyl, alkenyl, alkylaryl, or arylalkyl radical or a halogen atom;
- P is a stable non-coordinating or pseudo-non-coordinating anion;
- i is an integer having a value of 0 or 1;
- j is an integer having a value from 0 to 2;
- k is an integer having a value from 1 to 3; and
- l is an integer having a value from 0 to 2.

According to another aspect of the present invention there are provided ligand precursors of the bridged metal complexes of the invention, i.e., of those metal complexes of formula $YR''_iZ_jMeQ_kP_l$ where both i and j are 1, said ligand precursors being

represented by the general formula $YR^{\alpha}Z$ wherein Y, R^{α} and Z are as previously defined.

According to a further aspect of the present invention, there are provided catalyst systems for the polymerization of addition polymerizable monomers, particularly olefins, comprising the product obtainable by contacting:

- (A) a metal complex of the general formula $YR^{\alpha}_iZ_jMeQ_kP_l$ as described above, and
- (B) an activating cocatalyst.

The present invention also provides a process for polymerizing addition polymerizable monomers, particularly olefins, comprising contacting at least one addition polymerizable monomer with a catalyst comprising a metal complex of the general formula $YR^{\alpha}_iZ_jMeQ_kP_l$ according to the invention. For cationic catalysts of the general formula (i.e., $l=1$ or 2), an ion-pair or a strong Lewis acid compound is reacted with the neutral metallocene (i.e., $l=0$) to form a cationic metallocene either prior to or concurrent with contacting the catalytic system with monomer.

The present invention further provides a process for producing tactiospecific polymers comprising contacting at least one metallocene catalyst component of the general formula $YR^{\alpha}_iZ_jMeQ_kP_l$, where i is 1, j is 1, and Y and Z are as previously defined and further where Y and Z bear similar or different substituents in the α and β positions such that at least one β substituent is sterically bulkier than a hydrogen atom and particularly sterically bulkier than a methyl group. Metallocenes of the present invention where neither Y or Z are bilaterally or pseudo-bilaterally symmetric or where only one of them is bilaterally or pseudo-bilaterally symmetric and with the bulky β is on the non symmetric Y or Z radical will yield isoselective

catalysts. Such isoselective catalyst generally have overall C_2 or pseudo- C_2 symmetry as well. Metallocenes of the present invention where Y and Z are bilaterally or pseudo-bilaterally symmetric and have the bulky group on only one Y or Z will yield syndioselective catalysts and have overall C_s , or pseudo- C_s symmetry.

Furthermore, the catalyst components of the general formula may be made into pre-polymerized catalytic systems prior to contacting the system with the monomer and/or prior to the stabilization of the reaction conditions. Thus, the present invention provides also a process for polymerizing addition polymerizable monomers, comprising the steps of:

- (i) contacting a small amount of at least one addition polymerizable monomer with a catalyst as claimed in any of claims 16 or 17 to form a pre-polymer; and
- (ii) contacting the pre-polymer obtained in step (i) with one or more addition polymerizable monomers to form a polymeric product.

Moreover, the present invention can also be practiced to produce intimate blends of different types of polymers by contacting a catalyst of the general formula designed for each polymer type with one or more monomers. The preferred application of this invention is in the production of polyethylene, ethylene copolymers, isotactic polypropylene, syndiotactic polypropylene, hemi-isotactic polypropylene, propylene copolymers, or mixtures thereof.

According to a still further aspect of the present invention, there are provided methods for preparing the metal complexes of the invention, methods for preparing the ligand precursors of

said metal complexes, and methods for activating said metal complexes into catalytically active polymerization agents.

DETAILED DESCRIPTION OF THE INVENTION

The inventors have found that a new class of catalysts with wide application to the production of polymers of addition polymerizable monomers can be formed utilizing ligand systems containing at least one and up to three open-pentadienyl ligands where the open-pentadienyl ligands are delocalized, six π electron systems that are not constrained to a five membered ring. The present invention is directed towards catalytic systems and catalytic processes for the polymerization of addition polymerizable monomers. In particular, the present invention is directed towards catalytic systems and processes for the polymerization of polymerizable vinyl monomers, including α -olefins such as ethylene, propylene, butylene, and the like to polymers such as high molecular weight polyethylenes including linear low density polyethylene (LLDPE) and high density polyethylene (HDPE), polypropylene, isotactic polypropylene, syndiotactic polypropylene, hemi-isotactic polypropylene and the like and intimate mixtures thereof. The polymers are intended for fabrication into articles by extrusion, injection molding, thermoforming, rotational molding, and the like.

In particular, the polymers of this invention include homopolymers of ethylene, propylene, butylene, styrene, and other vinyl monomers and copolymers of these vinyl monomers where the vinyl monomers can have from 2 to about 20 carbon atoms and preferably 2 to 12 carbon atoms.

In the process of the present invention, a monomer such as ethylene or propylene, either alone or together with other C₂-C₂₀ monomers, is polymerized in the presence of a catalyst sys-

tem comprising at least one metallocene containing at least one Op ligand and optionally a co-catalyst such as an alumoxane.

In accordance with this invention, one can also produce olefin copolymers particularly copolymers of ethylene and/or propylene and other olefins by a judicious choice of metallocenes of the general formula. The choice of metallocenes of the present invention can be used to control comonomer content as well as other properties of the polymer such as tacticity for vinyl monomers other than ethylene or ethylene like monomers.

The term open-pentadienyl is intended to refer to all six π electron structures that are centered on five connected atoms in an all cis configuration, but where the five atoms bearing the six π electrons are not part of a five membered ring, i.e., the five atoms do not form a cyclopentyl ring system. Of course, all five atoms should preferably be sp_2 hybridized or in some other hybridization that can support electron delocalization.

One possible precursor to the Op ligands of this invention is a precursor where four of the atomic centers are part of two non-conjugated double bonds connected to and separated by a central atom, where the double bonds contribute two electron each to the ligand system which the central atom supplies two electrons to the system either directly as a lone pair of a N or P atom or through the loss of a removable group, such as a proton, to result in the formation of an anionic center as for a C or Si atom. Of course, other central species could be used as well including Ge, As and the like.

The numbers associated with the five atomic centers in formula (a) are there to indicate how substituent positions will be addressed in the remainder of the specification which is analogous to the numbering in cyclopentadiene, but not to the IUPAC

numbering convention for non-ring systems. Thus, for those metallocenes having a structural bridge, i.e., those metal complexes of formula (a) where i is 1, the structural bridge will be bonded to the central atom which is designated as position 1, in a fashion analogous to the numbering in cyclopentadiene. Additionally, the 2 and 5 positions will sometimes be jointly referred to as the α positions or proximal positions (proximal to the 1 position), while the 3 and 4 positions will sometimes be jointly referred to as the β or distal positions.

Open-pentadienyl ligands with one or two aromatic rings or ring systems supplying one or two pairs of electrons to the six π electron system form groups that are open analogs of such cyclic group as indene or fluorene ring systems as well as other open analogs of other aromatic species. These analogous open systems will be designated with an o- followed by a name or abbreviated name such as o-Ind (open-indene) and o-Flu (open-fluorene).

Especially suitable metal complexes according to the invention are the bridged compounds of formula $YR''ZMeQ_kP_l$, i.e. those of formula $YR''_iZ_jMeQ_kP_l$ wherein both i and j are 1, and where Y , R'' , Z , Me , Q , P , k , and l are as described above.

An important subclass of ligand systems and catalysts/catalyst precursors derived therefrom of this invention are represented by the formula $YR''ZMeQ_kP_l$, where Y is an Op containing radical as described above, Z is a Cp containing radical, a nitrogen containing radical, a phosphorous containing radical, an oxygen containing radical, a sulfur containing radical, or the like, and where R'' , Me , Q , P , k , and l are as described above. Non limiting examples of these compounds are:

isopropylidene(cyclopentadienyl)(1,5-bis(trimethylsilyl)pentadien-3-yl)zirconium dichloride;

dimethylsilanediyl(cyclopentadienyl)(1,5-bis(trimethylsilyl)-
pentadien-3-yl)zirconium dichloride;
isopropylidene(indenyl)(1,5-bis(trimethylsilyl)pentadien-3-yl)
zirconium dichloride;
dimethylsilanediyl(indenyl)(1,5-bis(trimethylsilyl)pentadien-3-
yl) zirconium dichloride;
isopropylidene(9-fluorenyl)(1,5-bis(trimethylsilyl)pentadien-3-
yl) zirconium dichloride;
dimethylsilanediyl(9-fluorenyl)(1,5-
bis(trimethylsilyl)pentadien-3-yl)zirconium dichloride;
isopropylidene(cyclopentadienyl)(6,6-dimethyl-cyclohexadien-3-
yl) zirconium dichloride;
dimethylsilanediyl(cyclopentadienyl)(6,6-dimethyl-cyclohexadien-
3-yl)zirconium dichloride;
isopropylidene(indenyl)(6,6-dimethylcyclohexadien-3-yl)zirconium
dichloride;
dimethylsilanediyl(indenyl)(6,6-dimethylcyclohexadien-3-yl)
zirconium dichloride;
isopropylidene(9-fluorenyl)(6,6-dimethylcyclohexadien-3-yl)
zirconium dichloride;
dimethylsilanediyl(9-fluorenyl)(6,6-dimethylcyclohexadien-3-yl)
zirconium dichloride.

Another important subclass of ligand systems and catalysts/catalyst precursors derived therefrom of this inven-
tion are represented by the formula $YR''ZMeQ_kP_l$, where Y is an Op
containing radical as described above, Z is the same or differ-
ent Op containing radical as described above, and where R'', Me,
Q, P, k, and l are as described above. Non limiting examples of
these compounds are:

isopropylidene-bis(1,5-bis(trimethylsilyl)pentadien-3-yl)zirconium dichloride;

dimethylsilanediyl-bis(1,5-bis(trimethylsilyl)pentadien-3-yl)zirconium dichloride;

isopropylidene-bis(6,6-dimethyl-cyclohexadien-3-yl)zirconium dichloride;

dimethylsilanediyl-bis(6,6-dimethyl-cyclohexadien-3-yl)zirconium dichloride.

A particularly suitable subclass of ligand systems and catalysts/catalyst precursors derived therefrom of this invention capable of producing polymers with varying degrees of tacticity are represented by the formula $YR''ZMeQ_kP_l$, where Y is a Op containing radical and Z is the same or different Op containing radical, a Cp containing radical, a nitrogen containing radical, a phosphorous containing radical, an oxygen containing radical, or a sulfur containing radical and where Y and Z are substituted with at least one non-hydrogen substituent so that the overall ligand or catalysts system has either C_s , C_2 , pseudo- C_s , or pseudo- C_2 symmetry and R'' , Me, Q, P, k, and l are as described above.

The present invention also provides a process for producing polymers and copolymers having varying and controllable properties including a high molecular weight at relatively high temperatures, tacticospecificity, low, medium and high molecular weights, stereoregularity, narrow or broad molecular weight distribution, etc. The process comprises polymerizing one or more monomers in the presence of one or more of the metallocenes described above. The advantages and novelties of this invention are obtained by the presence of a least one open-pentadienyl containing ligands in conjunction with other ligands to prepare

new metallocenes and catalysts therefrom in order to control and tailor polymer properties such as molecular weight, copolymer composition, molecular weight distribution, crystallinity, tacticity, melting point, T_g , etc.

The inventors have found that catalysts of the present invention can also be prepared which yield stereoregular and/or stereospecific polymer products such as linear high molecular weight polyethylene, isotactic polyolefins, syndiotactic polyolefins and hemi-isotactic polyolefins. These uniquely designed catalysts have as a key feature a ligand system containing two ligands, at least one being a Cp ligand and for tactic specific catalysts a given symmetry or pseudo-symmetry.

For stereospecific and/or tactic specific polyolefins, the catalysts of the present invention can be stereolocked and preferably stereorigid or geometrically constrained, in the case where the second ligand is a non-Cp or non-open-pentadienyl ligand, through the judicious choice of substituents and bridging groups where the substituents lock the polymer chain-end orientation and/or monomer approach such that each successive monomer addition is stereospecific or where the degree of stereoselectivity can be controlled. These catalyst are characterized by having two ligands (i.e., $j = 1$) and where at least one β or distal substituent or their equivalent (the group on a amine or phosphine anion ligand) on one ligand is sterically different from the β substituents on the other ligand and such that the overall ligand system has either C_s , C_2 , pseudo- C_s , or pseudo- C_2 symmetry.

The inventors have also found that by controlling the substituents relative steric size, catalysts can be formed that insert statistically controllable defects into the resulting

polymers. The inventors have also found that catalysts of the present invention can be designed to produce hemi-isotactic polymers. The inventors have also found that intimate mixtures of polymers with different properties can be prepared by polymerizing monomer in the presence of a combination of catalysts of the present invention or polymerizing monomer in the presence of catalysts of this invention in combination with prior art catalysts.

Traditionally, the term metallocene, in accordance with normal art usage, denotes an organometallic coordination compound in which two cyclopentadienyl containing ligands are coordinated to or "sandwiched" about a central metal species and where all five centers of the Cp ring are involved in metal coordination (haptic five coordinate ligands). The metal species may be a transition metal or transition metal halide, alkylide, alkoxide, or the like. Such structures are sometimes referred to as "molecular sandwiches" since the cyclopentadienyl ligands are oriented above and below a plane containing the central coordinated metal atom and nearly parallel to the planes containing the Cp ring. Similarly, the term "cationic metallocene" means a metallocene in which the central coordinated metal atom carries a positive charge, i.e., the metallocene complex is a cation associated with a stable non-coordinating or pseudo-non-coordinating anion.

However, in additions to the traditional meaning of the term metallocene, the present invention expands this term to encompass ligand systems where at least one of the ligands coordinating the central metal atom or ion is an open-pentadienyl containing ligand and the second ligand can be

another Op containing ligand, a Cp containing ligand, or a nitrogen, phosphorus, oxygen or sulfur containing ligand.

The metallocenes of the present invention can be either non-stereorigid/non-stereolocked, stereorigid/non-stereolocked, non-stereorigid/stereolocked, stereorigid/stereolocked, or mixtures thereof. Stereorigidity is imparted to the metallocene ligand systems of this invention by a chemical bridging group (R'') connecting the two ligands making up the metallocene, i.e., $i = 1$. The bridging group prevents the two ligands from undergoing structural isomerizations.

Suitable Y radicals for use in the present invention are those described in International applications WO 96/08497, WO 96/08498 and WO 96/16094, which are incorporated herein by reference. Preferably, in the formula (a), G is a carbon atom and J and J', same or different, are respectively a $CR^3R^{3'}$ and a $CR^4R^{4'}$ radical. Non limitative examples of Y radicals are: pentadien-3-yl, 1,5-bis(trimethylsilyl)pentadien-3-yl, cyclohexadien-3-yl, 6,6-dimethyl-cyclohexadien-3-yl, 1-trimethylsilyl-3-(1-cyclohexenyl)-propane.

Suitable Z radicals for use in the present invention include, without limitation, radicals represented as follows:

- Cp containing radicals represented by the general formula $(C_5R'_m)$ where $(C_5R'_m)$ is a cyclopentadienyl or substituted cyclopentadienyl radical, each R' is the same or different radicals as described above for radicals R^1 to R^5 or where two carbon atoms are joined together to form a C_4 - C_6 ring and m an integer having a value from 0 to 5;
- nitrogen and phosphorus containing radicals represented by the general formula (XR^6_m) where X is nitrogen or phosphorus atom, each R^6 is same or different radical as

described above for radicals R^1 to R^5 and m is an integer having a value from 1 to 3 (when n is 1, X carries a negative charge);

- an oxygen or sulfur containing radical represented by the general formula $(UR^7)_n$ where U is oxygen or sulfur atom and where R^7 is a radical as described above for radicals R^1 to R^5 and n is an integer having a value of 0 or 2 (when n is 0, then U carries a negative charge); or
- Op containing radicals with formula (a) described above.

Of course, one skilled in the art should also recognize that the permissible values for i , j , k , l , m , and n will depend on the actual ligand system and on the coordinating metal and these values are understood to conform to known organometallic structural and electronic requirements.

Suitable structural bridging groups R'' for use in this invention and impart stereorigidity to the metallocene catalysts of this invention include, without limitation, a C1-C20 alkenyl radical, a peralkylated C1-C20 alkenyl radical, a dialkyl methyl radical, a C3-C12 cyclohydrocarbyl radical, an aryl radical, a diarylmethylene radical, a diaryl allyl radical, a silicon hydrocarbyl radical, dihydrocarbyl silenyl radicals, a germanium hydrocarbyl radical, a phosphorous hydrocarbyl radical, a nitrogen hydrocarbyl radical, a boron hydrocarbyl radical, an aluminum hydrocarbyl radical, and the like.

Other suitable bridging groups R'' , include ionic units such as $B(C_6F_5)_2$, and $Al(C_6F_5)_2$, and the like and R_2C , R_2Si , R_4Et , R_6Pr , and the like where R can be any hydrocarbon, cyclic hydrocarbon, cyclic or linear hydrocarbons bearing another organometallic catalyst or carboranes, etc. Indeed, the bridges can be C_2 bridges (and C_3 etc.) which form the backbone of polymeric sup-

ports (e.g. the atactic, syndiotactic and isotactic polymers from vinyl-indene and 9-vinyl-fluorene etc.) as well as functionalized polystyrene precursors and all other polymers with terminal or branched boron or Al functional groups which are bonded to the catalysts, e.g., in zwitterionic form. R_2C and R_2Si bridging groups are preferred with isopropylidene and dimethylsilyl bridging groups being particularly preferred. Suitable radicals corresponding to R^1 through R^7 and R' include, without limitation, hydrogen atoms, linear or branched C1-C20 hydrocarbyl radicals, linear or branched C1-C20 halocarbyl radicals, linear or branched C1-C20 hydrohalocarbyl radicals, linear or branched C1-C20 alkoxy radicals, C3-C12 cyclohydrocarbyl radicals, a C3-C12 cyclohydrohalocarbyl radicals, aryl radicals, alkylaryl radicals, arylalkyl radicals, silicon hydrocarbyl radicals, germanium hydrocarbyl radicals, phosphorus hydrocarbyl radicals, nitrogen hydrocarbyl radicals, boron hydrocarbyl radicals, aluminum hydrocarbyl radicals, halogen atoms, and the like. Preferable, non-hydrogen radicals include linear or branched C1-C20 alkyl radicals with linear or branched C1-C10 radicals being particularly preferred and methyl, ethyl, isopropyl, t-butyl, and tri-alkylsilyl radicals being especially preferred.

Additionally, suitable radicals corresponding to R^1 through R^7 and R' include, without limitation, zwitterionic radicals such as $Cp-B(C_6F_5)_3^-$, $Cp-Al(C_6F_5)_3^-$, $Cp-Al(CF_3)_3^-$, $Cp-X-Al(C_6F_5)_3^-$, $Cp-X-B(C_6F_5)_3^-$, and the like are also suitable radicals, where X can represent an alkenyl group, alkenoxy group or the like. Metallocenes of this invention containing zwitterionic radicals on either one of the ligand making up the ligand system of the present invention and incorporating a group 4 metal for Me would

not need an independent and sometimes stereochemically interfering counterion (i.e., $l=0$). These zwitterionic radicals may also be suitable for mono and di cations of metal complexes of formula $YR''_iZ_jMeQ_kP_l$ where Me is a group 5 metal in the plus five oxidation state (Me(V)). They could even conceivably be used to create ion-pair catalysts with the normally neutral group 3 metals in the plus three oxidation state (Me(III)). In this case, one could obtain heterogeneous insoluble ion-pair systems for improved polymer particle size and morphology control.

Suitable metals corresponding to Me include, without limitation, Group 3, 4, or 5 elements from the Periodic Table of Elements, or Lu, La, Nd, Sm, Gd, and the like. Preferably, Me is a Group 4 or 5 metal and more preferably a Group 4 metal, and specifically titanium, zirconium or hafnium.

Suitable hydrocarbyl radical or halogen corresponding to Q include, without limitation, a linear or branched C1-C20 alkyl radical, an aryl radical, an alkylaryl radical, an arylalkyl radical, a F atom, a Cl atom, a Br atom, and an I atom. Q is preferably a methyl or halogen, and more particularly a chlorine atom.

Exemplary hydrocarbyl radicals are methyl, ethyl, propyl, butyl, amyl, isoamyl, hexyl, isobutyl, heptyl, octyl, nonyl, decyl, cetyl, 2-ethylhexyl, phenyl, and the like. Exemplary alkylene radicals are methylene, ethylene, propylene, isopropylidene, and the like. Exemplary halogen atoms include fluorine, chlorine, bromine and iodine and of these halogen atoms, chlorine is preferred. Exemplary of the alkylidene radicals is methylenidene, ethylenidene and propylenidene. Exemplary nitrogen containing radicals include amines such as alkyl amines, aryl amines, arylalkyl amines, and alkylaryl amines. Exemplary silyl

containing radicals include, dialkyl silenyl, trialkyl silyl and the like.

Suitable non-coordinating or pseudo-non-coordinating anions corresponding to P in the general formula $YR^i Z_j MeQ_k P_l$ include, without limitation, $[BF_4]^-$, $B(PhF_5)_4^-$, $[W(PhF_5)_6]^-$, $[Mo(PhF_5)_6]^-$ (wherein PhF_5 is pentafluorophenyl), $[ClO_4]^-$, $[S_nO_6]^-$, $[PF_6]^-$, $[SbR_6]^-$, $[AlR_4]^-$ (wherein each R is independently, a C1-C5 alkyl group preferably a methyl group, an aryl group, e.g. a phenyl or substituted phenyl group, or a fluorinated aryl and alkyl group). Tactiospecific metallocenes of the present invention (i.e., metallocenes that produce polymers with varying degrees of tacticity) are metallocenes of the general formula where $i = 1$ and $j = 1$ and are characterized by having C_2 or pseudo- C_2 for isoselective catalyst or C_s or pseudo- C_s symmetry for syndio selective catalyst with respect to the distribution with α and β substituents (or pseudo α and β substituents in the case of non Cp or Op ligands) in the ligand system. Said another way, C_s or pseudo- C_s symmetry is manifest in ligand systems where both Y and Z have bilateral or pseudo-bilateral symmetry with respect to a bisecting mirror plane. While, C_2 and pseudo- C_2 symmetry is manifest in ligand systems where only one ligands (i.e., Y or Z) has bilateral or pseudo-bilateral symmetry and the other ligand is not bilaterally or pseudo bilaterally symmetric. Preferably, at least one of the β substituents at least one of the ligands in the bridged metallocenes of the present invention should be sterically larger than hydrogen and particularly sterically larger than a methyl group. A substituents except possibly with the except of fluorine, are sterically larger than hydrogen for the purposes of this invention and fluorine is considered larger than hydrogen for the purposes of this invention

as well. Most substituents are also sterically bulkier than a methyl group and in particular all substituents with more than one atom with an atomic number greater than or equal to carbon or with two or more atoms with atomic numbers greater than or equal to boron are considered sterically bulkier than a methyl group.

Of the metallocenes of this invention, hafnocenes, zirconocenes and titanocenes are most preferred. Illustrative, but non-limiting, examples of these metallocenes which can be usefully employed in accordance with this invention are mono-open-pentadienyl titanocenes such as, open-pentadienyl titanium trichloride and substituted-open-pentadienyl titanium trichloride (i.e., R^1 , R^2 , R^3 , R^3' , R^4 , R^4' and R^5 are hydrogens, halogens, alkyls, haloalkyls, hydrohaloalkyls, and the like in the case of an all carbon Op ligands; R^1 , R^2 , R^3'' , R^4'' , and R^5 are hydrogens, alkyls, haloalkyls, hydrohaloalkyls, and the like in the case of the diimino ($C = NR$) or diphosphino ($C = PR$) Op ligands; and R^1 , R^2 , and R^5 are hydrogens, alkyls, haloalkyls, hydrohaloalkyls, and the like in the case of carbonyl ($C = O$) or thiocarbonyl ($C = S$) Op ligands), bis(open-pentadienyl) titanium diphenyl where the open-pentadienyl radical can be unsubstituted or substituted, carbenes represented by the formulas $Op_2Ti=CH_2 \cdot Al(CH_3)_2Cl$, $(Op)(Cp)Ti=CH_2 \cdot Al(CH_3)_2Cl$, $(Op)(UR_m^6)Ti=CH_2 \cdot Al(CH_3)_2Cl$ or $(Op)(XR_n^7)Ti=CH_2 \cdot Al(CH_3)_2Cl$, and derivatives of these reagents where the titanium moiety is $Ti=CH_2 \cdot Al(CH_3)_3$, $(TiCH_2)_2$, $Ti=CH_2 \cdot AlR_2Cl$, wherein Op is an open-pentadienyl ligand or a substituted open-pentadienyl ligand, Cp is a cyclopentadienyl or substituted cyclopentadienyl radical, and R is an alkyl, aryl or alkylaryl radical having from 1-18 carbon atoms; substituted bis(Op)Ti(IV), (Op)(Cp)Ti(IV),

(Op)(UR⁶_m)Ti(IV) or (Op)(XR⁷_n)Ti(IV) or compounds such as bis(o-Ind)Ti, (Ind)(o-Ind)Ti, (o-Ind)(UR⁶_m)Ti or (o-Ind)(XR⁷_n)Ti diphenyl or dichloride, bis(o-Flu)Ti, (o-Flu)(Flu)Ti, (o-Flu)(UR⁶_m)Ti or (o-Flu)(XR⁷_n)Ti diphenyl or dihalides and other dihalide complexes where R⁶, R⁷, m and n are as described previously; multiply substituted Op systems and multiply substituted Op and multiply substituted Cp or UR⁶_m or XR⁷_n mixed systems such as bis(1,2-dimethyl-Op)Ti diphenyl or dichloride, bis(1,2-diethyl-open-Op)Ti diphenyl or dichloride and other dihalide complexes; silicone, phosphine, amine or carbon bridged Op containing ligand system complexes, such as dimethyl silyl bis(Op), (Op)(Cp), (Op)(UR⁶_m) or (Op)(XR⁷_n) titanium diphenyl or dichloride, methyl phosphine bis(Op), (Op)(Cp), (Op)(UR⁶_m) or (Op)(XR⁷_n) titanium diphenyl or dichloride, methylene bis-(Op), (Op)(Cp), (Op)(UR⁶_m) or (Op)(XR⁷_n) titanium diphenyl or dichloride, ethylene bis(4,5,6,7-tetrahydro-O-Ind), (4,5,6,7-tetrahydroindenyl)(4,5,6,7-tetrahydro-O-Ind), (4,5,6,7-tetrahydro-O-Ind)(UR⁶_m) or (4,5,6,7-tetrahydro-O-Ind)(XR⁷_n) titanium dichloride and other dihalide complexes and the like.

Illustrative, but non-limiting, examples of the zirconocenes which can be usefully employed in accordance with this invention are mono-open-pentadienyl zirconocenes such as, open-pentadienyl zirconium trichloride and substituted-open-pentadienyl zirconium trichloride (i.e., R¹, R², R³, R^{3'}, R⁴, R^{4'} and R⁵ are hydrogens, halogens, alkyls, haloalkyls, hydrohaloalkyls, and the like in the case of an all carbon Op ligands; R¹, R², R^{3''}, R^{4''}, and R⁵ are hydrogens, alkyls, haloalkyls, hydrohaloalkyls, and the like in the case of the diimino (C = NR) or diphosphino (C = PR) Op ligands; and R¹, R², and R⁵ are hydrogens, alkyls, haloalkyls,

hydrohaloalkyls, and the like in the case of carbonyl ($C = O$) or thiocarbonyl ($C = S$) Op ligands), bis(Op), (Op)(Cp), (Op)(UR⁶_m), or (Op)(XR⁷_n) zirconium diphenyl or dimethyl or dihalide, all substituted analogs thereof; silicone, phosphorus, and carbon bridged analogs such as dimethylsilyl bis(Op), (Op)(Cp), (Op)(UR⁶_m) or (Op)(XR⁷_n) zirconium dimethyl or dihalide, methylphosphine bis(Op), (Op)(Cp), (Op)(UR⁶_m) or (Op)(XR⁷_n) zirconium dimethyl or dihalide, and methylene bis(Op), (Op)(Cp), (Op)(UR⁶_m) or (Op)(XR⁷_n) zirconium dimethyl or dihalide, carbenes represented by the formula bis(Op), (Op)(Cp), (Op)(UR⁶_m) or (Op)(XR⁷_n) $Zr=CH_2P(C_6H_5)_2CH_3$, and derivatives of thereof.

The present invention also encompasses Hf, La, Lu, Sm, Nd, and Gd analogs of the above zirconocenes and titanocenes.

A few exemplified but not-limiting examples of metallocene ligands (AYZ) that generate catalysts with varying degrees of isotactic selectivity would include, without limitation: *rac*-R"(bis(3-R-1-Op)), *rac*-R"(3-R-1-Op)(3-R-1-Cp), *rac*-R"(3-R-Op)(XR⁶_m), *rac*-R"(3-R-Op)(UR⁷_n), *rac*-R"(bis(3-R-4-R'-1-Op)), *rac*-R"(bis(3-R-4-R'-1-Op)(3-R-4-R'-1-Cp)), *rac*-R"(bis(3-R-1-Op)), *rac*-R"(3-R-Op)(3-R-1-Cp), *rac*-R"(3-R-Op)(XR⁶_m), and *rac*-A(3-R-Op)(UR⁷_n), *rac*-R"(bis(3-R-4-R'-1-Op)), and *rac*-R"(bis(3-R-4-R'-1-Op)(3-R-4-R'-1-Cp)); *rac*-R"(bis(3-R-1-o-Ind)), *rac*-R"(3-R-1-o-Ind)(3-R-1-Ind), *rac*-R"(3-R-1-o-Ind)(XR⁶_m), *rac*-R"(3-R-1-o-Ind)(UR⁷_n); *rac*-R"(o-Flu)(3-R-Op), *rac*-R"(o-Flu)(3-R-1-Cp), *rac*-R"(o-Flu)(XR⁶_m), *rac*-R"(o-Flu)(UR⁷_n), and the like where R", X, U and R⁶⁻⁷ are as previously described, R and R' are as previously described for R¹⁻⁵, and where R is sterically larger than R'.

A few exemplified examples of metallocene ligands (AYZ), that generate catalyst with varying amounts of syndiotactic selectiv-

ity would include, without limitation, $R''(3,4\text{-di-R-1-Op})(Op)$, $R''(3,4\text{-di-R-1-Op})(Cp)$, $R''(3,4\text{-di-R-1-Op})(3',4'\text{-di-R'-1-Op})$, $R''(3,4\text{-di-R-1-Op})(3',4'\text{-di-R'-1-Cp})$, $R''(3,4\text{-di-R-1-Cp})(3',4'\text{-di-R'-1-Op})$, $R''(Op)(o\text{-Flu})$, $R''(Op)(Flu)$, $R''(3,4\text{-di-t-butyl-Op})(Flu)$, $R''(3,4\text{-di-t-butyl-Cp})(o\text{-Flu})$, $R''(3\text{-o-Ind})(Op)$, $R''(3\text{-Ind})(Op)$, $R''(3\text{-o-Ind})(Cp)$, and the like, where R'' is as previously describe, and R and R' are as previously described for R^{1-5} , and where R is sterically larger than R' .

The unique and novel feature of the catalysts of the present invention are that the catalysts include at least one non-cyclopentadienyl six π electron ligand system which singly or in combination with a second such ligand, a Cp containing ligand, a nitrogen containing ligand, a phosphorus containing ligand, an oxygen containing ligand or a sulfur containing ligand can produce metallocene catalysts that are capable of producing all manners and types of polyolefin containing polymers including polymers where the polyolefins have varying to high degrees of stereoregularity.

Indeed, the present catalysts can be tailored using a number of strategies to control properties such as the relative stereospecificities of the polymer products produced, the molecular weight of the polymer products produced, and other significant polymer properties. The single carbon bridged metallocenes have been shown to be more stereospecific than the silicon bridged analogs for syndiotactic specific catalysts; the carbon bridged metallocenes are generally less stereospecific than the silicon bridged analogs for isospecific catalysts. It is thought that the larger the steric requirements are for the β -substituents, the more stereospecific the catalyst is. The difference in the steric requirements for the β -substituent can

be used to optimize the orientation of the chain end which substituents at the α -position should result in increased polymer molecular weight.

The present invention is directed to both neutral metallocene and cationic metallocene catalysts and catalyst precursors as evidenced by the subscript 1 associated with the anion P having permissible values of 0 to 2, i.e., when $l=0$, the catalysts are neutral and when $l=1$ or 2 the catalysts are cationic.

The catalysts of the present invention can also be designed to produce polymers with very high tacticity indices depending on the desired tacticity. In order to produce the tactically specific catalysts and/or catalyst precursors of the present invention, the characteristics of the α and β substituents on the bridged ligands are important. Thus, the "steric requirement" or "steric size" of the α and β substituents are designed to control the steric characteristics of the catalyst/catalyst precursor such that the overall ligand system has C_2 or C_s or pseudo- C_2 or pseudo- C_s symmetry. This very specific arrangement of the α and β substituents allows control of the stereochemistry of each successive monomer addition.

The term C_s or pseudo- C_s symmetry means that the α and β substituents on each ligand are identical or similar, but for tactic selectivity it is necessary that the β -substituents on one ligand are sterically larger than the β -substituents on the other ligand. For example, the *rac*-isopropylidenebis(3-*t*-butyl-1-Op) ligand or the *rac*-isopropylidene(3-*t*-butyl-1-Op)(3'-*t*-butyl-1'-Cp) ligand would generate *rac* isospecific catalysts with C_2 ; the *rac*-isopropylidene(3-*t*-butyl-1-Op)(3'-*t*-butyl-4'-methyl-1'-Op) ligand or the *rac*-isopropylidene(3-methyl-4-*t*-butyl-1-Op)(3-*t*-butyl-1-Cp) ligand would generate *rac*

isoselective (less isospecific) catalysts with pseudo- C_2 symmetry (the *meso* isomer yields atactic polymer and can be separated from the *rac* catalyst by crystallization or other separation techniques well known in the art), while the isopropylidene(3,4-di-*t*-butyl-1-Op)(Op) ligand or the isopropylidene(3,4-di-*t*-butyl-1-Op)(Cp) ligand or isopropylidene(3,4-di-*t*-butyl-1-Cp)(Op) ligand or isopropylidene(3-*t*-butyl-1-Op)(ps-flu) ligand or related ligand would generate a syndiospecific catalyst with C_s or pseudo- C_s symmetry. Additionally, active isoselective catalysts can be prepared for having one ligand characterized by bilateral or pseudo bilateral symmetry while the other ligand is not bilaterally or pseudo-bilaterally symmetric. Of course, for syndiospecific catalysts, both ligands preferably are bilaterally or pseudo bilaterally symmetric.

A preferred class of Op ligands are those Op ligands where all five atomic centers are carbon atoms and where the 1, 3, and 4 positions of the Op ligand are substituted with bulky substituents such as iso-propyl groups, *t*-butyl groups, trialkylsilyl groups, and other similar bulky substituents. It is thought that such bulky groups stabilize the Op system. It may also be possible to strategically arrange substituents with the proper steric properties on an appropriate carbon(s) of the open-fluorene ring(s) of, e.g., R_2Si and Et bridged bis-open-fluorenyl complexes or mixed open-fluorene/fluorene complexes, which should serve as chain end conformational locks (preferably positioned in the mouth of the Flu ligand) and which could also confer solubility (ion pair separation for better catalyst activity and stereospecificity) and/or insolubility (for better control of polymer morphology); as desired. The bridged, substituted bis-open-fluorenyl or mixed open-

fluorenyl/fluorenyl complexes are stereorigid, provide chain-end conformational locks, and are superior to those without such conformational locks.

Prior art has shown, for example, that a methyl substituent positioned at the α -Cp position on the C5 ring of bisindenyl catalysts increases the molecular weight of isotactic polypropylene produced with the $\text{Et}[\text{Ind}]_2\text{ZrCl}_2$ based catalyst. Similarly, a methyl substituent on the C6 ring of the indenyl ring system has reduced the stereospecificity; depending on the positional isomerism. These effects can be reasonably expected to carry over to the catalyst system of the present invention. Also, the addition of methyl, t-Bu, OMe, Ph, etc. substituents to the o-Flu or Flu C6 ring and to the bridging group R" have had steric, solubility, and electronic influences on catalysts in syndiotactic and isotactic specific polymerizations. These effects are likewise expected to be carried over to metallocenes of the present invention and to their mixtures with other catalysts. Similarly the effects of substituting Al for B in the anions and the differences between carboranes and methylalumoxanes and other counter anions are reasonably expected to be carried over to the new catalyst systems described herein.

By making the sterically larger β -substituents different and/or the sterically smaller β -substituents different, the tactiospecific versions of the catalysts/catalyst precursors of the present invention can be designed to impart any degree of tacticity to the resulting polymers. Thus, if one β -substituent is t-butyl and another is ethyl, and the other two are hydrogens, the tactiospecificity of the catalyst system will be

duced relative to the one having two t-butyls and two hydrogens.

The concept of substituents with different steric requirements, size or bulk is well known in the art. However, to ensure that ordinary artisans understand its usage in the context of this invention, a non-exhaustive and illustrative list of the relative steric bulk of a variety of substituents can be found in Stoughtan and Adams article in J. Am. Chem. Soc., 54, 4426 (1932) and Yuan and Adams article in J. Am. Chem. Soc. 54, 4434 (1932).

Of course, cationic metallocene catalysts and catalyst precursors require the anion P to maintain net neutrality in the overall catalytic agent. The anion indicated by P in the general formula is preferentially a compatible non-coordinating or pseudo-non-coordinating anion that either does not coordinate with the metallocene cation or is only weakly coordinates to the metallocene cation to remain sufficiently labile so that it can be really displaced by a neutral Lewis base such as a monomer unit. Compatible non-coordinating or pseudo-non-coordinating anions are described as anions that stabilize the cationic metallocene catalyst systems, but do not transfer an anionic substituent or fragment to the cation to form a neutral metallocene and a neutral byproduct of the non-coordinately anion.

The useful size of the counterion P will also depend on the bulkiness or steric requirements of the substituent groups on the ligands of this invention. In addition to size, it is also thought that other characteristics are important for good anionic counterions. Such characteristics include stability and bonding. The anion must be sufficiently stable so that it can-

not be rendered neutral by virtue of the metallocene cation extracting an electron. The bond strength with the cation is such that it does not interfere with monomer coordination and chain propagation.

A preferred procedure for producing cationic metallocene catalyst of the present invention ($l=1$ or 2) involves the reaction of an ion-pair in a non-coordinating solvent with a metallocene of the general formula where $l=0$, with one or more Lewis acids or P precursor agents. Thus, triphenylcarbenium tetrakis(pentafluorophenyl) boronate may be reacted with a neutral metallocene of the present invention in a solvent such as toluene to generate a cationic metallocene of the present invention. This preparation method was referenced in U.S. Pat. No. 5,225,550, incorporated by reference.

A preferred application of the present invention is in the polymerization of alpha olefins, specifically ethylene and propylene, into all manners of polymers including linear medium and high density polyethylene, atactic, isotactic, syndiotactic, hemi-isotactic polypropylenes or mixtures thereof. However, the invention may be employed in the preparation of hemi-isotactic, isotactic or syndiotactic polymers derived from other ethylenically unsaturated monomers. For example, syndiospecific, isospecific or hemi-isotactic specific polymers of 1-butene, 1-pentene, 1-hexene, styrene or the like.

Addition polymerizable monomers suitable for use in this invention are ethylenically unsaturated monomers including, without limitation, any organic molecule having a terminal vinyl group ($\text{CH}_2=\text{CH}-$) such as: α -olefins including propylene, 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene and the like; vinyl halides including vinyl fluoride, vinyl chloride, and the

like; vinyl arenes including styrene, alkylated styrenes, halogenated styrenes, haloalkylated styrenes and the like; dienes such as 1,3-butadiene and isoprene (i.e., 1,2-addition). Polypropylene is probably of the greatest practical significance and the invention will be described in detail with reference to the production of polypropylene polymers of different tacticities. However, other polymers in which polymers having a desired tacticity are also of interest. These catalysts may also be useful in the polymerization of dienes to elastomers through the inclusion of 1,4-addition instead of 1,2-addition. Of course, these catalysts may also be useful in varying the relative amounts of 1,2-addition versus 1,4-addition polymers containing conjugated diene monomers. The term addition polymerizable monomer means all monomers that are polymerizable in an addition polymerization process with Ziegler, Ziegler-Natta, or Natta type transition metal polymerization catalysts. Activating cocatalysts suitable as component (B) in the catalysts of the invention are organo-aluminum compounds and, particularly alumoxanes. Alumoxanes are considered to be linear, branched or cyclic polymeric compounds which can be represented by the general formulae $(R--Al--O)_n$ which is a cyclic compound and $R(R--Al--O--)_n AlR_2$, which is a linear compound. In the general formula R is an alkyl group such as, for example, methyl, ethyl, propyl, butyl and pentyl and n is an integer from 1 to about 20. Examples of alumoxanes suitable for use according to the present invention are methylalumoxanes (MAO), isobutylalumoxanes and 2,4,4-trimethylpentylaluminumoxanes. Mixtures of different alumoxanes can also be used. Generally, in the preparation of alumoxanes from, for example, aluminum trimethyl and water, a mixture of the linear and cyclic

compounds is obtained. The alumoxane can be prepared in various ways. Preferably, they are prepared by contacting water with a solution of aluminum trialkyl, such as, for example, aluminum trimethyl, in a suitable organic solvent such as benzene or an aliphatic hydrocarbon. For example, the aluminum alkyl is treated with water in the form of a moist solvent. In an alternative method, the aluminum alkyl such as aluminum trimethyl can be desirably contacted with a hydrated salt such as hydrated copper sulfate. Preferably, the alumoxane is prepared in the presence of a hydrated copper sulfate. The method comprises treating a dilute solution of aluminum trimethyl in, for example, toluene, with copper sulfate represented by the general formula $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. The ratio of copper sulfate to aluminum trimethyl is desirably about 1 mole of copper sulfate for 4 to 5 moles of aluminum trimethyl. The reaction is evidenced by the evolution of methane.

The ratio of aluminum in the alumoxane to total metal in the metallocenes can be in the range of about 0.5:1 to about 10,000:1, and preferably about 5:1 to about 1000:1.

Activating cocatalysts suitable as component (B) in the catalysts of the invention are also the product of the reaction between water and an organometallic aluminum compound. Particularly suitable are the organometallic aluminum compounds of formula (II) described in EP-A-575,875 and those of formula (II) described in WO 96/02580, the relevant parts of both applications being incorporated in the present description. Non-limiting examples of those organometallic aluminum compounds are:

tris(isobutyl)aluminum,
bis(isobutyl)aluminum hydride,

methyl-bis(isobutyl)aluminum,
dimethyl(isobutyl)aluminum,
tris(isohexyl)aluminum,
tris(benzyl)aluminum,
tris(tolyl)aluminum,
tris(2,4,4-trimethylpentyl)aluminum,
bis(2,4,4-trimethylpentyl)aluminum hydride,
isobutyl-bis(2-phenyl-propyl)aluminum,
diisobutyl-(2-phenyl-propyl)aluminum,
isobutyl-bis(2,4,4-trimethylpentyl)aluminum,
diisobutyl-(2,4,4-trimethylpentyl)aluminum.

Mixtures of different organometallic aluminum compounds and/or alumoxanes can also be used.

Further activating cocatalysts suitable as component (B) in the catalysts of the invention are those compounds capable of forming an alkyl zirconocene cation. Non-limiting examples of these compounds are the ionic compounds consisting of a cation which is a Bronsted acid capable of donating a proton and of reacting irreversibly with a substituent Q of the metal complex of the invention, and of a compatible anion which does not coordinate, which is capable of stabilizing the active catalytic species originating from the reaction of the two compounds, and which is sufficiently labile to be able to be displaced from an olefinic substrate. The anion preferably comprises one or more boron atoms. More preferably, the anion is of formula $\text{BAr}_4^{(-)}$, wherein the Ar substituents, same or different, are aryl radicals such as phenyl, pentafluorophenyl, bis(trifluoromethyl)phenyl. Tetrakis-pentafluorophenyl borate is particularly preferred. Moreover, compounds of formula BAr_3 can be used conveniently.

The polymerization procedures disclosed in U.S. Pat. No. 4,892,851, may be also employed in carrying out the methods of the present invention and is incorporated herein by reference. The solvents used in the preparation of the catalyst system are inert hydrocarbons, in particular a hydrocarbon that is inert with respect to the catalyst system. Such solvents are well known and include, for example, isobutane, butane, pentane, hexane, heptane, octane, cyclohexane, methylcyclohexane, toluene, xylene and the like. As a further control and refinement of polymer molecular weight, one can vary the concentration of alumoxane. Higher concentrations of alumoxane in the catalyst system results in higher polymer product molecular weight.

The catalyst systems described herein are suitable for the polymerization of olefins in solution, slurry or gas phase polymerizations and over a wide range of temperatures and pressures. For example, such temperatures may be in the range of about -60°C to about 280°C and especially in the range of about 50°C to about 160°C . The pressures employed in the process of the present invention are those well known for, for example, in the range of about 1 to about 500 atmospheres and greater. In a solution phase polymerization, the alumoxane is preferably dissolved in a suitable solvent, typically in inert hydrocarbon solvent such as toluene, xylene, and the like in molar ratios of about $5 \times 10^{-3}\text{M}$. However greater or lesser amounts can be used. The solid catalysts in combination with an alumoxane can be usefully employed in slurry and gas phase olefin polymerizations.

After polymerization and deactivation of the catalyst, the product polymer can be recovered by processes well known in the art

for removal of deactivated catalysts and solution. The solvents may be flashed off from the polymer solution and the polymer obtained extruded into water and cut into pellets or other suitable comminuted shapes. Pigments, antioxidants and other additives, as is known in the art, may be added to the polymer. The polymer product obtained in accordance with this invention will generally have a weight average molecular weight in the range of about 1,400,000 to about 500 and preferably 500,000 to about 1000. The polydispersities (molecular weight distribution) expressed as M_w/M_n are typically from 1.5 to 4, but can be higher. The polymers can contain 1.0 chain end unsaturation per molecule. Broadened MW can be obtained by employing two or more of the metallocenes of this invention in combination with the alumoxane. The polymers produced by the process of this present invention are capable of being fabricated into a wide variety of articles, as is known for polymer products derived from addition polymerizable monomers. While the applicant's invention is not to be restricted by theory, it is believed that neutral metallocenes form cationic complexes by reaction with the MAO in the manner as disclosed by Zambelli, A. et al., "Isotactic Polymerization of Propene: Homogenous Catalysts Based on Group 4 Metallocenes Without Methylaluminoxane", *Macromolecules* 1989, 22, pages 2186-2189. The catalyst precursors used in the present invention may be prepared by procedures similar to those disclosed in U.S. Pat. No. 4,892,851, while the active cationic catalysts may be produced by simply converting the neutral metallocene into the cationic state following procedures such as those disclosed in European applications 277,003 and 277,004 or by reaction with triphenylcarbenium boronates. Similarly, alcohol - $B(PhF_5)_3$

complexes can be used as anionic precursors for forming the active cationic metallocenes of the present invention where the alcoholic proton reacts with an amine of an alkyl group on the coordinating metal atoms to generate a cationic metallocene and an alkoxide - $B(PhF_5)_3$ anion. For additional information see, A.R. Siedle, W.M. Lammana, R.A. Newmark, J. St. Werrs, D.E. Richardson, M. Ryan, Makromol Chern, Masroonal Symp. 66, 215 (1993).

The soluble, homogeneous catalysts of this invention can also be converted to supported heterogeneous catalysts by depositing the catalysts on supports including, without limitation, silica, alumina, magnesium dichloride, polystyrene beads, and like. The supported analogs of the present catalyst can improve the bulk density of the polymer as further described in Canadian Pat. No. 2,027,145, U.S. Pat. Nos. 4,935,474 and 4,530,914 and European Appln. Nos. 0,427,697 and 0,426,638, incorporated herein by reference.

The catalysts of the invention can also be chemically linked to the support by placing functional groups with ion pairs or Lewis acid centers or Lewis base centers on the ligands and/or supports. Supporting can also be achieved by using large (oligomeric or polymeric) insoluble anions as counter ions. Additionally, the catalysts of the present invention can be used to prepare low, moderate and high molecular weight polymers, low, moderate and high density polymers, elastomers, aspecific, isospecific, syndiospecific, hemi-isospecific, and/or aspecific polymers, not only of propylene, but for all α -olefins such as 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, $CH_2=CH(CH_2)_pSi(CH_3)_3$ where p is 1 to 4, and the like. Additionally, the catalysts of this invention can polymerize

singly or in mixtures all addition polymerizable monomer including vinyl monomers and diene monomers. One of ordinary skill should recognize that the ligands that can give rise to isoselective catalysts will give rise to a *meso* form which is asymmetric and a *rac* form that is selective to specific to isotactic polymers. The stereospecific *rac* catalysts can be separated from the *meso* form by crystallization. Perhaps we should also mention that it is well known from the Bercaw et al. work (Reference: J. Am. Chem. Soc. 1992, 114, 7607 J.E. Bercaw and E.B. Coughlin.) in the prior art that *rac*-metallocenes free of the undesirable aspecific *meso* stereoisomers can be prepared by placing suitable bulky substituents such as $\text{Si}(\text{Me})_3$ on the ligand atoms proximal to (α to) the bridgehead atom.

The catalysts of the present invention can obviously be used in conjunction with each other, all other metallocene catalysts, $\text{TiCl}_3/\text{DEAC}$, and or $\text{TiCl}_4/\text{MgCl}_2/\text{TEAL}$ catalysts having internal electron donors such as diisobutylylphthalate and external donors such as diphenyldimethoxysilane, methanol, etc. to produce polymers with mixed stereochemical compositions, distributions or tailored molecular weight distributions. Reactor blends of polymers with optimized physical, thermal, mechanical, and rheological properties can be tailored to produce the optimum mixture for specific applications requiring high melt strength, high clarity, high impact strength, and high rates of crystallization, simply by mixing catalyst species together in appropriate ratios.

The catalysts of the present invention clearly have the potential to influence the rate of termination by β -hydride elimination reactions. This, therefore, provides a novel ligand effect for controlling polymer molecular weights. These cata-

lysts can be exploited to tailor molecular weights and hence molecular weight distributions with mixed species of the catalysts and any other class of catalysts. This would be advantageous in tailoring the polymer properties in HDPE, LLDPE, i-PP, s-PP, etc. Similarly the chain-end conformation locking substituent will influence the rate of reactivity of the new metallocenes with α -olefins such as propylene, butene and hexene. The new ligand effects on the catalyst reactivity ratios can be exploited to produce reactor blends with varying compositions, sequences, distributions and/or molecular weight distributions. Similarly, the catalysts can reasonably be expected to provide improved tailored grades of polypropylene and propylene-ethylene high impact copolymers as reactor blends or from reactors in series including fluidized and stirred gas phase polymerizations.

The catalysts of the present invention can also be used to generate copolymers of olefins and copolymers of olefins and dienes with varying degrees of tactiospecificity.

The generalized methods that follow describe the preparation of the catalyst and/or catalyst precursors and active catalysts. It is important that the catalyst complex be "pure" as low molecular weight, amorphous polymer can be produced by impure catalysts.

Generally, the preparation of the metallocene complex consists of forming and isolating the ligand system (bridged or unbridged) which are then aromatized or deprotonated to form delocalized electron systems or hetero anions and reacted with a metal halide, alkylide, or the like to form the complex.

The synthetic procedures are generally performed under an inert gas atmosphere using a glove box or Schlenk techniques. The

synthesis process generally comprises the steps of: (1) preparing the halogenated or alkylated metal compound, (2) preparing the ligand, (3) synthesizing the complex, and (4) purifying the complex.

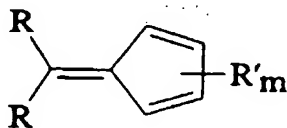
The synthesis of Op's generally involves the reaction of a suitable 1,4-di-unsaturated compound directly with the metal species or with a strong base to render the delocalized six π electron anionic system and then reacting the anionic species with the metal species. In the case of bridged ligand systems of the present invention, the 1,4-di-unsaturated compounds are first reacted with a strong base such as lithium alkyl to produce the anion which can then be reacted with dialkyl dihalo silicon to produce silicon bridged ligand bis (Op) systems or with a fulvene to produce mixed Op-R"-Cp systems.

For hetero systems such as those containing one or more CN double bonds, CO double bonds, CP double bonds, or CS double bonds, the precursor reagents would be preferably reacted with strong basis such as an alkyl sodium, alkyl potassium, alkylaluminum, or similar reagents or with lithium metal, sodium metal or potassium metal to prevent addition to the hetero double bond.

Suitable 1,4-di-unsaturated compounds include 1,4-pentadiene and all substituted analogs thereof provided the C3 carbon has at least one hydrogen atom so that the system can be render anionic through deprotonation; 1-aryl-pent-2-enes, 1,1-diarylmethanes, α - γ or 1,3 diketones, dialdehydes, dithioketone, and dithioaldehydes (i.e., compounds represented by $U=CR-CHR-CR=U$ where R is a hydrogen or any other substituent and U is O or S), α - γ or 1,3 diimines or diphospines (i.e., compounds represented by $RX=CR-CHR-CR=XR$ where R is a hydrogen or any other

substituent and X is N or P); and analogs thereof where the C3 carbon atom is replaced by a N or P atom.

The synthesis of the β -substituted Cp ligands of the present invention can be accomplished by contacting an appropriately substituted fulvene with an appropriately substituted open-cyclopentadienyl containing anion under reaction conditions sufficient to produce a bridged structure having the requisite β -substituents on the Cp ring and the Op ligand to yield ligand systems with either C_2 or C_s or pseudo C_2 or pseudo C_s symmetry. Fulvene is cyclopentadiene with an exo-cyclic methylene group at the 1 position of cyclopentadiene ring. The exo-cyclic methylene carbon is the 6 position of fulvene. Since this carbon can ultimately become the bridging group R" in the formula $YR''_i Z_j MeQ_k P_l$, the preferred fulvenes for the preparation of the present catalysts are typically 6,6-disubstituted fulvenes so that the resulting bridging group is a tertiary carbon atom. The fulvenes useful in preparing the ligands of the present invention have substituents in the 3 and 4 positions Q and are generally 6,6 disubstituted, while the other sites can be substituted or unsubstituted as shown below:



where R'_m are as previously described and where the R groups and the exocyclic carbon (C6 in fulvene) is meant to be the precursor to the structural bridging group R".

As noted previously, a preferred mode of converting the neutral metallocenes to cationic metallocene catalyst useful in the present invention involves reaction of the neutral metallocenes with a triphenylcarbenium boronate. A preferred reactant is triphenylcarbenium tetrakis (pentafluorophenyl) boronate.

The catalysts of the present invention can also be made into efficient pre-polymerized catalysts by the methods disclosed in U.S. Pat. Nos. 3,893,989, 4,200,171, 4,287,328, 4,316,966 and 5,122,583 incorporated herein by reference. Essentially, the catalysts are used to polymerize monomer on a small scale to form a catalyst with a low molecular weight polymer surrounding and stabilizing the catalyst. The pre-polymerized catalysts can be prepared in the presence of co-catalysts such as the ones described previously and optionally in the presence of various electron donors.

The pre-polymerized catalysts can then be introduced into a reaction zone containing monomer. The resulting polymerization can show greatly improved catalytic efficiencies. The preferred method for using pre-polymerized catalysts of the present invention is contacting a pre-polymerized metal complex according to the invention with a co-catalyst and introducing the catalyst into a polymerization reaction zone containing monomer. Of course, the pre-polymerized catalysts can be introduced into the reaction zone in a stream either separately or in conjunction with separate streams containing the co-catalyst and/or electron donors.

Preferred pre-polymerized catalysts of the present invention have a weight ratio of polymer/catalyst of approximately 0.1-100 with ratios of less than 10 being particularly preferred. The

syntheses are conveniently done at room temperature or lower in low boiling solvents which are readily evaporated *in vacuo*.

A general scheme of preparing the metal complexes of the invention is outlined below for the synthesis of $(\text{CH}_3)_2\text{Si}(\text{o-Flu})(\text{Cp})_2\text{ZrCl}_2$ as a catalyst precursor.

Equal amounts of 1,1-diphenyl methane and Cp are reacted with one molar equivalence of an alkyl lithium such as methyllithium, n-butyllithium, or sec-butyllithium. To this 1 to 1 mixture of 1,1-diphenyl methyl anion and CpLi is added 1/2 equivalent of $(\text{CH}_3)_2\text{SiCl}_2$. The mixture makes three different ligands: bis(Cp) $(\text{CH}_3)_2\text{Si}$, (Cp)(o-Flu) $(\text{CH}_3)_2\text{Si}$, and bis(o-Flu) $(\text{CH}_3)_2\text{Si}$. These ligands can be separated by standard separation techniques. The (Cp)(o-Flu) $(\text{CH}_3)_2\text{Si}$ or (O-Flu) $(\text{CH}_3)_2\text{Si}$ system can then be reaction with two molar equivalent of an alkyl lithium to produce the dianion which is then reacted with ZrCl_4 to form the desired metallocene.

The preparation for the non-aromatic containing Op ligands proceeds by reacting 1,5-di(trimethylsilyl)-1,4-pentadiene with an alkyl lithium reagent to which can be added 6,6-dimethylfulvene to form the isopropylidenyl(Cp)(3,4-di(trimethylsilyl)Op) ligand system. This ligand system can then be reacted with two equivalents of alkyl lithium to form the dianion which can be reacted with ZrCl_4 .

Thus, while in accordance with the patent statutes, the best mode and preferred embodiments of the invention have been described, it is to be understood that the invention is not limited thereto, but rather is to be measured by the scope and spirit of the appended claims. The following examples are given by way of illustration of the invention and are not to be construed as limiting.

EXAMPLE 1(1) Synthesis of (9-fluorenyl)(4,4-dimethylcyclohexadien-1-yl)
(dimethyl)silane

35 mmol of butyllithium (1.6 M solution in hexanes, 22 mL) were added slowly to a solution of 5,5-dimethyl-1,3-cyclohexadiene (35 mmol, 3.85 g) in THF (10 mL) and stirred overnight to give a solution of lithium 6,6-dimethylcyclohexadienide. (5,5-dimethyl-1,3-cyclohexadiene was prepared as described previously by P.T. DiMauro and P.T. Wolczanski, *Organometallics* 1987, 6, 1947-1954.) Chlorodimethyl(9-fluorenyl)silane was prepared in situ as follows: 30.5 mmol of phenyllithium (1.8 M solution in cyclohexane-ether (70 : 30), 17 mL) were added slowly to a solution of fluorene in ether (70 mL) at room temperature. After stirring overnight, solvents were removed in vacuo and the residue was washed with pentane. The resulting yellow solids were mixed with 60 mL of pentane, cooled to -78°C, and 60 mmol of dichlorodimethylsilane (7.3 mL) were added by syringe. After slowly warming the reaction flask to room temperature over the course of several hours, solvents and residual dichlorodimethylsilane were removed in vacuo. The product was dissolved in 60 mL of ether without removing the LiCl and the lithium 6,6-dimethylcyclohexadienide solution described above was added slowly at -30 C via cannula. After stirring overnight at room temperature, the reaction was quenched with 20 mL of a saturated NH₄Cl solution. The aqueous layer was extracted with ether (2 x 20 mL) and the combined organic fractions were washed with water (2 x 20 mL), dried over MgSO₄, filtered, and evaporated to an orange oil (9.20 g). The oil was chromatographed on silica gel using a 9 : 1 hexane-methylene chloride solvent mixture. Following a short run of an unidenti-

fied light oily product, 3.60 g of the title product were isolated as a colorless oil. Mass spectrum (m/e RA): 330(0.3), 223(100), 195(69), 165(23), 59(9.0). $^1\text{H-NMR}$ (CDCl_3) δ , ppm: 7.9 (d, 2 H), 7.5 (d, 2 H), 7.3 (m, 4 H), 5.4 (m, 4 H), 4.05 (s, 1 H), 2.4 (m, 1 H), 1.06 (s, 3 H), 1.03 (s, 3 H), 0.0 (s, 6 H).

(2) Synthesis of dimethylsilanediyl(9-fluorenyl)(6,6-dimethylcyclohexadien-3-yl)zirconium dichloride

6.7 mmol butyllithium (1.6 M solution in hexanes, 4.2 mL) were added slowly at 0 C to a solution of (9-fluorenyl)(4,4-dimethylcyclohexadien-1-yl)(dimethyl)silane (3.3 mmol, 1.10 g) in THF (2 mL). After stirring at room temperature for 6 h, solvents were removed in vacuo and the oily residue was washed with pentane (15 mL). The dianion was dissolved in ether (15 mL) and added slowly to 3.0 mmol of ZrCl_4 (0.70 g) in pentane (15 mL) at -78°C . After stirring overnight at room temperature, solvents were removed under reduced pressure and the residue extracted with toluene and filtered. Evaporation of the filtrate and addition of pentane gave 0.20 g of the title product.

(3) Ethylene polymerization

In a glove box, 10 mg of dimethylsilanediyl(9-fluorenyl)(6,6-dimethylcyclohexadien-3-yl)zirconium dichloride were dissolved in 1.5 mL of MAO (10 wt. % solution in toluene, Witco Chemical Corp.), stirred for 5 minutes, and diluted with 40 mL of toluene containing 1.5 mL of MAO. The solution was transferred to a dry pressure bottle equipped with magnetic stirrer and temperature bath and pressurized to 3 bar with ethylene. After stirring for 15 minutes at 25 C, the pressure was released and water (3 mL) was syringed into the slurry. The reactor contents were washed with a 50:50 methanol - 4 N HCl solution (3 x 50

mL), water (3 x 50 mL), and filtered. The solids were washed with methanol and dried under reduced pressure to yield 2.5 g of polyethylene (intrinsic viscosity = 3.01 dL/g).

EXAMPLE 2

(1) Synthesis of trimethylsilyl-1,4-pentadiene

A solution containing 1,4-pentadiene (5 g, 73 mmol) in diethylether (100 mL) was lowered to -78°C and n-butyllithium was added dropwise (72 mmol, 1.6M soln. in hexanes, 45 mL). The flask was stirred overnight and the temperature was allowed to warm to ambient. Solvents were removed in vacuo and a bright yellow powder was isolated. The sample was then re-dissolved in fresh diethyl ether (100 mL) and the temperature was lowered to -78°C. Trimethylchlorosilane (7.9 mmol, 10 mL) was added dropwise. The reaction was allowed to slowly warm to ambient and the flask contents stirred overnight. Solvents were removed in vacuo. ¹H-NMR: (THF-d₈), d, ppm; 6.25 (m, 2H), 5.9 (m, 2H), 5.65 (m, 2H), 4.95 (s, 1H), 4.90 (s, 1H), 4.80 (s, 1H), 4.75 (s, 1H), 1.5 (d, 2H), 0 (m, 9H).

(2) Synthesis of bis(1,5-trimethylsilyl)-1,4-pentadiene

A 250 mL reaction flask was charged with n-butyllithium (72 mmol, 1.6M soln. in hexanes, 45 mL) and the temperature was lowered to -78°C. A solution containing trimethylsilyl-1,4-pentadiene (73 mmol, 10.2 g, prepared above) in THF (20 mL) was added dropwise. The solution was allowed to warm to room temperature and stirred overnight. The solution separated into two layers upon standing, the bottom layer was collected and washed with pentane. The bottom layer prepared in this fashion was then dissolved in THF (70 mL) and the temperature reduced to -78°C. Trimethylchlorosilane (7.9 mmol, 10 mL) was added dropwise to the stirred solution and the temperature was allowed

to rise to ambient overnight. The reaction was then concentrated in vacuo to 30 mL and washed with pentane. The pentane solution was collected and the pentane removed in vacuo to produce 4.72 g of a straw colored liquid. ¹H-NMR (major isomer): (THF-d₈) δ, ppm; 6.5 (m, 1H), 5.95 (m, 1H), 5.75 (m, 1H), 5.5 - 5.6 (m, 1H), 1.57 (d, 2H), 0.3 (s, 9H), 0.0 (s, 9H). Mass spectrum (m/e (RA): 212 (3.17), 124 (30.3), 109 (50.1), 73.1 (100), 59 (15.6), 45.1 (22.1), 43.1 (10.3).

(3) Synthesis of 2-cyclopentadienyl-2-(1,5-bis(trimethylsilyl)pentadien-3-yl)propane

A 100 mL reaction flask was charged with bis(1,5-trimethylsilyl)-1,4-pentadiene (30 mmol, 6.36 g) in THF (25 mL), cooled to -78°C, and treated with butyllithium (30 mmol, 2.5 M solution in hexanes, 12 mL). After stirring at room temperature for 15 h, the temperature was lowered to -78°C and 6,6-dimethylfulvene (30 mmol, 3.19 g) in THF (15 mL) was added dropwise. The flask and contents were warmed to room temperature over a 2 h period. After stirring at room temperature for 3 h, the reaction mixture was treated with a saturated ammonium chloride solution (20 mL). The aqueous layer was extracted with ether (2 x 20 mL) and the combined organic fractions were washed with water (2 x 20 mL), dried over MgSO₄, filtered, and evaporated to an oil. The crude material was distilled (ca. 100 C, 0.02 mm) giving 5.47 g of the title product as a light yellow oil. Mass spectrum (m/e RA): 318(2.96), 107(100), 91.1(21.2), 73(31.34), 45(7.86).

(4) Synthesis of isopropylidene(cyclopentadienyl)(1,5-bis(trimethylsilyl)pentadien-3-yl)zirconium dichloride

A 100 mL reaction flask was charged with 2-cyclopentadienyl-2-(1,5-bis(trimethylsilyl)pentadien-3-yl)propane (6.9 mmol, 2.2g)

in pentane (10 mL), cooled to -78°C , treated with potassium *t*-butoxide (14 mmol, 1.0 M solution in THF, 14 mL), butyllithium (14 mmol, 1.6 M solution in hexanes, 8.8 mL), and stirred for 1 h. The flask and contents were slowly warmed to room temperature and stirred an additional 1.5 h. Solvents were removed in vacuo and the residue was washed by stirring in pentane. After removing the pentane, toluene (20 mL) was added, the flask and contents were cooled to -78°C , and ZrCl_4 (6.9 mmol, 1.61g) in toluene (15 mL) was added via cannula. The flask and contents were stirred overnight at room temperature. Solvents were removed under reduced pressure and the resulting red-brown solids were used without further purification.

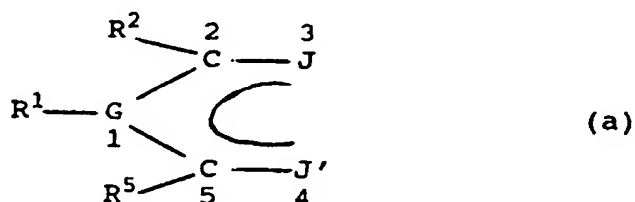
(5) Ethylene polymerization

In a glove box, 15 mg of isopropylidene(cyclopentadienyl)-(1,5-bis(trimethylsilyl)pentadien-3-yl)zirconium dichloride were dissolved in 30 mmol of MAO (20 wt. % solution in Isopar C, 11.7 mL) and placed on a shaker. After 10 minutes, the catalyst solution and ethylene gas were charged to a 4 L stainless steel autoclave containing 2 L of hexane stirring at room temperature. The reactor temperature was raised to 70°C in 5 minutes with controlled ethylene flow to give a final pressure of 150 psi. After stirring for 2 hours at 150 psi, the ethylene pressure was vented and the reactor cooled to room temperature. The hexane slurry was poured into a separate flask, washed with a 50:50 methanol - 4 N HCl solution (100 mL), water (100 mL), and filtered. The solids were dried in a vacuum oven to yield 22 g of polyethylene (intrinsic viscosity = 9.3 dL/g).

CLAIMS

1. A metal complex represented by the general formula $YR''_iZ_jMeQ_kP_l$ wherein:

- Y is an open-pentadienyl containing radical of the formula (a):



where G is a carbon atom, a nitrogen atom, a silicon atom or a phosphorus atom; J is a $CR^3R^{3'}$ radical, a $SiR^3R^{3'}$ radical, a $NR^{3''}$ radical, a $PR^{3''}$ radical, an oxygen atom or a sulfur atom and J' is a $CR^4R^{4'}$ radical, a $SiR^4R^{4'}$ radical, a $NR^{4''}$ radical, a $PR^{4''}$ radical, an oxygen atom or a sulfur atom and where J and J' can be the same or different; R^1 , R^2 , R^3 , $R^{3'}$, $R^{3''}$, R^4 , $R^{4'}$, $R^{4''}$, and R^5 can be the same or different and are a hydrogen atom, a linear or branched C1-C20 hydrocarbyl radical, a linear or branched C1-C20 halocarbyl radical, a linear or branched C1-C20 hydrohalocarbyl radical, a linear or branched C1-C20 alkoxy radical, a C3-C12 cyclohydrocarbyl radical, a C3-C12 cyclohydrohalocarbyl radical, an aryl radical, an alkylaryl radical, an arylalkyl radical, a silicon hydrocarbyl radical, a germanium hydrocarbyl radical, a phosphorous hydrocarbyl radical, a nitrogen hydrocarbyl radical, a boron hydrocarbyl radical, an aluminum hydrocarbyl radical or a halogen atom, or R^2 and R^3 , $R^{3'}$ or $R^{3''}$ and/or R^5 and R^4 , $R^{4'}$ or $R^{4''}$ can be joined together to form a 4 to 6 membered ring or a

fused 6 to 20 membered ring system, or where R^3 , $R^{3'}$, or $R^{3''}$ and R^4 , $R^{4'}$, or $R^{4''}$ can be joined together so that the five numbered atonic centers making up the five centered delocalized six π electron ligand are contained in a 7 to 20 membered ring, or where R^3 , $R^{3'}$, or $R^{3''}$ and R^4 , $R^{4'}$, or $R^{4''}$ can be fused together so that the five numbered atonic centers making up the five centered delocalized six π electron ligand are contained in a six membered ring;

- Z is the same of different Op containing radical, a Cp containing radical, a nitrogen containing radical, a phosphorous containing radical, an oxygen containing radical, a sulfur containing radical, or the like;
- R'' is a C1-C20 alkenyl radical, a peralkylated C1-C20 alkenyl radical, a C3-C12 cyclohydrocarbyl radical, an aryl radical, a diaryl allyl radical, a silicon hydrocarbyl radical including a dihydrocarbyl silenyl radical, a germanium hydrocarbyl radical including a dihydrocarbyl germanium radical, a phosphorous hydrocarbyl radical including a phosphine radical, a nitrogen hydrocarbyl radical including an amine radical, a boron hydrocarbyl radical, an aluminum hydrocarbyl radical, or the like, and where R'' structurally bridges the Y radical and a Z radical;
- Me is a Group 3, 4, or 5 element from the Periodic Table of Elements, or Lu, La, Nd, Sm, Gd, or the like;

- Q is a C1-C20 hydrocarbon radical such as an aryl, alkyl, alkenyl, alkylaryl, or arylalkyl radical or a halogen atom;
 - P is a stable non-coordinating or pseudo-non-coordinating anion;
 - i is an integer having a value of 0 or 1;
 - j is an integer having a value from 0 to 2;
 - k is an integer having a value from 1 to 3; and
 - l is an integer having a value from 0 to 2.
2. The metal complex of claim 1, wherein i is 1 and j is 1.
3. The metal complex of claim 2, wherein Z is a Cp containing radical, a nitrogen containing radical, a phosphorous containing radical, an oxygen containing radical, a sulfur containing radical, or the like.
4. The metal complex of claim 2, wherein Z is an Op containing radical and Y and Z are the same or different.
5. The metal complex of claim 2, wherein Y and Z are substituted with at least one non-hydrogen distal or β substituent so that the metallocenes yield polymers with varying degrees of tacticselectivity for monomers other than ethylene.
6. The metal complex of claim 2, wherein YR"Z has at least one β substituent sterically larger than a hydrogen atom on either Y or Z and where said metallocenes generate polymers with varying degrees of tacticselectivity for monomers other than ethylene.
7. The metal complex of claim 2, wherein both Y and Z are bilaterally or pseudo-bilaterally symmetric and where

- Y or Z has at least one β substituent larger than hydrogen and where said metallocene has overall C_s or pseudo- C_s symmetry and produced polymers with varying degrees of syndioselectivity for monomers other than ethylene.
8. The metal complex of claim 2, wherein either both Y and Z are not bilaterally or pseudo-bilaterally symmetric or where only one Y or Z is bilaterally or pseudo-bilaterally symmetric and where Y or Z has at least one β substituent larger than hydrogen and produced polymers with varying degrees of syndioselectivity for monomers other than ethylene.
 9. The metal complex of claim 8, wherein said metal complex has overall C_s or pseudo- C_s symmetry.
 10. The metal complex of any of claims 1 to 9, wherein in the formula (a) or radical Y, G is a carbon atom and J and J', same or different, are respectively a $CR^3R^{3'}$ and a $CR^4R^{4'}$ radical.
 11. The metal complex of claim 10, wherein Y is a radical selected from the group consisting of pentadien-3-yl, 1,5-bis(trimethylsilyl)pentadien-3-yl, cyclohexadien-3-yl, 6,6-dimethyl-cyclohexadien-3-yl and 1-trimethylsilyl-3-(1-cyclohexenyl)propane.
 12. The metal complex of any of claims 1 to 9, wherein the R" bridging group is selected from the group consisting of isopropylidene and dimethylsilylenyl groups.
 13. The metal complex of any of claims 1 to 9, wherein Me is selected from the group consisting of titanium, zirconium and hafnium.

14. The metal complex of any of claims 1 to 9, wherein Q is selected from the group consisting of a methyl radical and a chlorine atom.
15. A ligand precursor of the metal complex of claim 2, said ligand precursor being represented by the general formula YR^mZ wherein Y, R^m and Z are as defined in any of claims 1 to 12.
16. A catalyst system for the polymerization of addition polymerizable monomers, particularly olefins, comprising the product obtainable by contacting:
- (A) a metal complex of the general formula $YR^m_iZ_jMeQ_kP_l$ as claimed in any of claims 1 to 14, and
- (B) an activating cocatalyst.
17. The catalyst system of claim 16, wherein the activating cocatalyst is an organo-aluminum compounds and, particularly, an alumoxane.
18. A process for polymerizing addition polymerizable monomers, particularly olefins, comprising contacting at least one addition polymerizable monomer with a catalyst as claimed in any of claims 16 or 17.
19. The process of claim 18, wherein the addition polymerizable monomers are selected from the group consisting of ethylene, α -olefins, such as propylene, 1-butene, 1-hexene and 1-octene, cycloolefins and conjugated diolefins.
20. A process for polymerizing addition polymerizable monomers, comprising the steps of:
- (i) contacting a small amount of at least one addition polymerizable monomer with a catalyst as

claimed in any of claims 16 or 17 to form a pre-polymer; and

- (ii) contacting the pre-polymer obtained in step (i) with one or more addition polymerizable monomers to form a polymeric product.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 96/03952

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C07F17/00 C08F10/00 C08F4/60

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C07F C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	ORGANOMETALLICS, vol. 8, 1989, pages 105-109, XP000564728 YAMAMOTO H.: "structural features in electron deficient Me ₅ CpTi-diene complexes..." see page 108, column 1; examples 6A,3A; table II see page 106, column 1; examples 6A,6B ---	1,10,13, 14
X	J. AM. CHEM. SOC., vol. 104, 1982, pages 3737-3739, XP002021170 LIU ZHENG : "Bis(2,4-dimethylpentadienyl)titanium: an open titanocene" see the whole document ---	1,10,13

-/--

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

17 December 1996

Date of mailing of the international search report

14. 01. 97

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+ 31-70) 340-3016

Authorized officer

Fischer, B

INTERNATIONAL SEARCH REPORT

Internat'l Application No
PCT/EP 96/03952

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE,A,43 37 230 (BASF) 4 May 1995 see claims 5,6 see page 2, line 22 - page 3, line 34 ---	1
X	US,A,3 577 448 (DEFFNER JOHN) 4 May 1971 see abstract see claim 1 see column 5; example II ---	1
X	PATENT ABSTRACTS OF JAPAN vol. 18, no. 122 (C-1173), 28 February 1994 & JP,A,05 310828 (MITSUBISHI) see abstract ---	1,16-19
P,X	JP,A,08 081 516 (MITSUBISHI) 26 March 1996 see abstract ---	1,16-19
P,X	WO,A,96 08498 (THE DOW CHEMICAL) 21 March 1996 cited in the application see claims 1-6,8,9,15 see page 30 - page 34; example 1 see page 39; example 8 ---	1-3,6-8, 10-19
P,X	WO,A,95 33776 (SPECS AND BIOSPECS) 14 December 1995 see claims 11-17,20,21 see page 17 - page 18; example 18 ---	1,13-19
A	ORGANOMETALLICS, 1995, pages 3132-3134, XP000566147 DEVORE DAVID D.: "Constrained-geometry titanium diene complexes" see page 3133, column 1; example 2B -----	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 96/03952

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE-A-4337230	04-05-95	EP-A- 0652224 JP-A- 7188272	10-05-95 25-07-95
US-A-3577448	04-05-71	NONE	
JP-A-8081516	26-03-96	NONE	
WO-A-9608498	21-03-96	US-A- 5541349	30-07-96
WO-A-9533776	14-12-95	NL-A- 9400919 NL-A- 9401515 AU-A- 2579895	02-01-96 01-05-96 04-01-96

